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Occurrence and abundance of 6-methyl branched glycerol dialkyl glycerol tetraethers in soils: Implications for palaeoclimate reconstruction

Cindy De Jonge*, Ellen C. Hopmans, Claudia I. Zell, Jung-Hyun Kim, Stefan Schouten, Jaap S. Sinninghe Damsté

Department of Marine Organic Biogeochemistry, NIOZ Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg (Texel), The Netherlands

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Abstract

The distribution of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in soils has been shown to correlate with the soil pH and the mean annual air temperature (MAT). This has been used to perform palaeoclimate reconstructions based on brGDGTs recovered from palaeosoils, freshwater, and marine sedimentary archives. Recently described 6-methyl brGDGTs were shown to co-elute with the 5-methyl brGDGTs that are used to calculate the CBT and MBT′ indices used as palaeoclimate proxies. The impact of these 6-methyl brGDGTs on the established palaeoclimate proxies is unknown and will depend on their abundance in soils. Using improved chromatography, we quantified the fractional abundance of 6-methyl brGDGTs in globally distributed soils and show that they are abundant components, comprising on average 24% of the total amount of brGDGTs. All penta- and hexa-methylated brGDGTs (i.e. with zero to two cyclopentane moieties) were shown to comprise both 5- and 6-methyl isomers. The fractional abundances of the six 6-methyl brGDGTs correlate positively with each other, suggesting a common biological source in most soils, and correlate strongly with soil pH. The presence of the 6-methyl brGDGTs introduced scatter in the original MBT′/CBT-MAT calibration and caused a dependence on soil pH of the MBT′. Exclusion of the 6-methyl brGDGTs from the MBT′, i.e. the newly defined $\mathrm{MBT}'_{5\mathrm{ME}}$, shows that it is no longer related to soil pH. The correlation with MAT is improved, reducing the residual mean error (RMSE) from 6.2 to 4.8 °C. Also, the correlation of the CBT after the exclusion of the 6-methyl brGDGTs (defined as $\mathrm{CBT}_{5\mathrm{ME}}$) with soil pH slightly improved. Furthermore, the separate quantification of the 6-methyl brGDGTs allows the definition of new indices. The CBT′, which comprises the 6-methyl brGDGTs, is a substantially improved alternative to the $\mathrm{CBT}_{5\mathrm{ME}}$, reducing the RMSE from 0.8 to 0.5 pH units. Also, the accuracy of MAT reconstructions can be improved using a multiple linear regression, the $\mathrm{MAT}_{\mathrm{mr}}$, decreasing the RMSE further to 4.6 °C. Furthermore, we introduce an index that allows the reconstruction of MAT in sites where only the ubiquitous brGDGT Ia, IIa and IIIa are present, the $\mathrm{MAT}_{\mathrm{mrs}}$. Our results imply that separate quantification of the 6- and 5-methyl brGDGT is essential for accurately quantifying brGDGTs in environmental samples and results in substantially improved MAT and soil pH reconstructions.

1. INTRODUCTION

A challenge in continental palaeoclimate research is the development of quantitative climate proxies that can be applied in continuous records. These archives can be found,

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* Corresponding author. Tel.: +31 222369562.
E-mail address: cindy.de.jonge@nioz.nl (C. De Jonge).

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for example, in calcite deposits in caves (e.g. Gascoyne, 1992) or in lakes, where undisturbed sedimentation can occur over long timespans, up to 6.7 Ma (Kravchinsky et al., 2003). A large part of the continental temperature records is indeed retrieved from lake sediments, where climate indicators like pollen may be preserved, together with chironomids or diatoms, whose community changes record the temperature of the lake water (e.g. Smol and Cumming, 2000; Broström et al., 2008; Eggermont and Heiri, 2012). The number of proxies that can estimate past continental air temperatures, however, is relatively limited.

The distribution of a set of 9 bacterial lipids, branched glycerol dialkyl glycerol tetraethers (brGDGTs), has been demonstrated to show a relationship with mean annual air temperature (MAT) and soil pH (Weijers et al., 2007b). This observation has led to the development of a continental palaeoclimate proxy, with applications in palaeosoils (Peterse et al., 2009a, 2011) and speleothems (Blyth and Schouten, 2013). Following soil erosion and run-off through rivers, the soil-derived brGDGTs can also be recovered from marine and lake sediments (e.g. Weijers et al., 2007a; Niemann et al., 2012), where their incorporation in sediments creates a continuous palaeoclimate archive. BrGDGT lipids are stable components that can persist in the environment up to at least 55 Ma (Weijers et al., 2011a).

Our knowledge of the structural diversity of brGDGTs has been developed just over the past decade (Schouten et al., 2013a). In 2000, the structure of the two dominant brGDGTs has been elucidated using NMR (Sinninghe Damsté et al., 2000; Ia and IIa; see Fig. 1 for structures), after their isolation from a Dutch Holocene peat bog. Unlike the GDGTs of archaea, the alkyl core chain was not isoprenoidal, but shown to be a straight chain comprising two to three methyl groups. These alkyl core chains can undergo internal cyclization, resulting in the presence of one or two cyclopentane moieties (Weijers et al., 2006; Ib–c, IIb–c, IIIb–c). Both the non-isoprenoidal structure and the stereo-configuration of the glycerol moieties indicated a bacterial origin (Weijers et al., 2006). Acidobacteria, that occur in substantial cell numbers in soil and peat (e.g. Fierer et al., 2007), were proposed as likely candidates (Weijers et al., 2009). The observation that brGDGT concentrations in soils are higher at lower pH fits with the higher abundance of subdivision 1 Acidobacteria in soil at lower pH (Peterse et al., 2010). Recently, brGDGT Ia has been detected in two cultured Acidobacterial strains from subdivision 1 (Sinninghe Damsté et al., 2011). However, although usually a full suite of 9 brGDGTs is present in the environment, only one brGDGT has been recovered from a bacterial culture so far and this mismatch still remains to be explained.

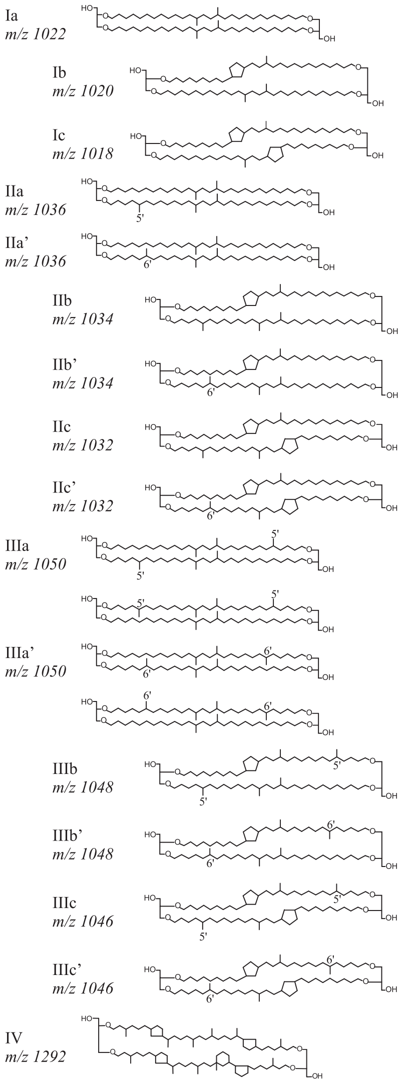

Fig. 1. Chemical structures of branched GDGTs (I-III) and crenarchaeol (IV). BrGDGTs Ia, Ib and Ic are referred to as 'tetra-methylated', brGDGTs IIa, IIa′, IIb, IIb′, IIc and IIc′ are referred to as 'penta-methylated', brGDGTs IIIa, IIIa′, IIIb, IIIb′, IIIc and IIIc′ are referred to as 'hexa-methylated' brGDGTs. The compounds that have one or two methyl groups at the α and/or ω-6 position are indicated with a prime symbol, and are referred to as 6-methyl brGDGTs. The compounds that have one or two methyl groups in the α and/or ω-5 position are referred to as 5-methyl brGDGTs. The chemical structures of the hexa- and penta-methylated brGDGTs with cyclopentyl moiety(ies) IIb′, IIc′, IIIb′ and IIIc′ are tentative.

BrGDGTs are abundant lipids found in soils and peat across the globe (Weijers et al., 2006; Peterse et al., 2010; Yang et al., 2013). As the precursor organisms thrive in highly contrasting soil conditions, the composition of the lipid membrane is variable in order to adjust the membrane fluidity to different environments. The relative distribution of the nine brGDGTs in a global soil dataset, expressed in the Methylation of Branched Tetraethers (MBT) and Cyclisation of Branched Tetraethers (CBT) ratios, was shown to correlate with the ambient MAT and soil pH (Weijers et al., 2007b). These authors hypothesized that the temperature has a direct effect on membrane fluidity, while the soil pH will affect the proton gradient across the membrane. Based on an extended soil dataset (Peterse et al., 2012), the MBT was simplified by removing two minor components (brGDGT IIIb and IIIc) and redefined as the MBT′. However, when reconstructing the MAT